

Photoemission study of polycrystalline $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$: correlation and surface effects

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We report photoemission studies of polycrystalline samples of Sr-doped $\text{GdTiO}_{3+\delta}$, which undergoes a Mott-Hubbard-like metal-insulator transition at a Ti-concentration of $\approx 20\%$. The Ti $3d$ -derived valence band near the Fermi level displays a two-peak structure consistent with a Hubbard-model-type interpretation as quasiparticle and lower Hubbard band. Contrary to the theoretical expectation the lower Hubbard band does not change its energy with doping. However, the analysis of the core level spectra and elemental mapping with a scanning electron microscope indicate a strongly inhomogeneous doping concentration in the probed surface regions. This questions the intrinsic character of the valence band spectra and demonstrates a general difficulty when using polycrystalline samples for such studies.

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Many transition metal oxides display metal-insulator transitions (MITs) upon variation of external parameters such as temperature, pressure, or chemical doping. These result from a competition between local Coulomb interactions in the open metal $3d$ shell and electron delocalization induced by hopping via the oxygen ligands.¹ A particularly simple class of systems are the perovskite-like titanates RTiO_3 , where R denotes a trivalent rare earth ion such as Y^{3+} or La^{3+} . This leaves the Ti-ion in a $3d^1$ state and should according to band theory result in a metallic ground state. However, the strong on-site $3d$ Coulomb energy turns the undoped material into a Mott-insulator.¹ Replacing the trivalent R -ions by divalent ions reduces the Ti $3d$ occupation from an integer value and eventually restores the metallic state beyond a critical doping level. Such MITs have been investigated in detail for, e.g., $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ and $\text{Y}_{1-x}\text{Ca}_x\text{TiO}_3$.^{2,3}

The physics of the Mott transition is theoretically best described within the Hubbard model framework. Recently, enormous progress has been made in its treatment to allow detailed calculations of physical properties which can be compared to experiment.^{1,4,5,6} The most direct test of the theory concerns its spectral properties. For example, the single-particle excitation spectrum (or rather its electron removal part) can in principle be probed by photoelectron spectroscopy.⁷ Photoemission studies on early transition metal perovskites with doping-induced MITs^{8,9,10,11,12,13} indeed confirm some of the predictions of the Hubbard model. For example, they observe a characteristic double-peak structure of the Ti $3d$ spectrum which is consistent with the expected splitting into a quasiparticle peak and an incoherent lower Hubbard band. On the other hand, there are also qualitative discrepancies between theory and photoemission, concerning especially the effect of doping on the energy of these spectral features. One has to keep in mind though that photoemission is an extremely surface sensitive method and that these studies have been performed on scraped surfaces of polycrystalline material. Very little is known about quality, atomic geometry, defect density, or homogeneity of these surfaces.

Here we present photoemission results on $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ which also displays a doping-induced MIT.¹⁴ The Ti $3d$ spectra are similar to those observed in other titanates and display overall qualitative agreement with calculated Hubbard model spectra. However, from peculiar charging effects in the core level spectra we find that the doping concentration in the probed surface layer is non-homogeneous. Chemical microanalysis by scanning electron microscopy confirms this result. These findings invalidate any interpretation of the valence band spectra as those of a single-phased compound and question the use of polycrystalline material for such studies.

The low energy properties of $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ have been studied in detail in Ref. 14. Undoped GdTiO_3 is a Mott insulator which at low temperatures undergoes ferrimagnetic ordering. Hole-doping by substituting Sr for Gd leads to an insulator-metal transition at $x \approx 0.2$. In the metallic regime the low energy properties are observed to follow Fermi liquid-type behavior at least up to $x = 0.5$. Approaching the Mott transition from the metallic side the Sommerfeld coefficient of the specific heat increases up to 50 times with respect to simple metals. This indicates a strong enhancement of the effective carrier mass and thus the formation of heavy fermion quasiparticles.¹⁴ Upon further doping, a second MIT occurs slightly above $x = 0.7$ concomitant with a structural change from orthorhombic to cubic symmetry. Pure SrTiO_3 is a band insulator.

Ceramic samples of $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ have been calcinated from TiO_2 , SrCO_3 , Gd_2O_3 and Ti_2O_3 high purity powders and pressed into pellets. These pellets have been annealed at 1200°C under N_2 atmosphere for 15 hours and finally arc-melted under argon atmosphere. From thermogravimetric measurements the amount of excess oxygen was found to be $\delta \approx 0.3$, except for $x = 0.6$ and 0.8 where $\delta = 0.12$ and 0.06 , respectively. Assuming formal valencies of Gd^{3+} , Sr^{2+} , and O^{2-} the nominal occupation of the Ti $3d$ shell is given by $n_{3d} = 1 - x - 2\delta$. The samples used here are identical to the ones studied in Ref. 14.

Valence band spectra were obtained by ultraviolet photoelectron spectroscopy (UPS) using He I radiation (21.2 eV). For x-ray photoemission (XPS) of the core levels we used monochromatized Al K_{α} radiation (1486.6 eV). The energy resolution was 45 meV and 1.3 eV for UPS and XPS, respectively. Clean surfaces of the polycrystalline samples were prepared by *in situ* scraping with a diamond file. The cleanliness of the surfaces was characterized by the absence of a C 1s signal and by a well-defined O 1s peak.

A typical UPS valence band spectrum of $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ is shown in Fig. 1. The intense feature below -4 eV is formed by bands of predominantly O 2p character. The small emission closer to the Fermi level is attributed to Ti 3d states.⁹ Its lineshape displays a characteristic double structure with a broad feature centred at -1.3 eV and a sharp much less intense peak at the Fermi level. By analogy to the valence band spectra of other titanates^{8,9,10,13} and by comparison to theoretical spectra (discussed below) these structures are identified as lower Hubbard band (LHB) and quasiparticle band (QP), respectively.

The evolution of the Ti 3d spectrum with Sr-doping is shown in Fig. 2(a). In order to facilitate better comparison the spectra have been normalized to same integral area; without this normalization the spectral Ti 3d weight decreases relative to the O 2p signal, in line with the reduced 3d occupancy. All spectra display the characteristic decomposition into a LHB peak and a quasiparticle band. The latter is most intense for high doping

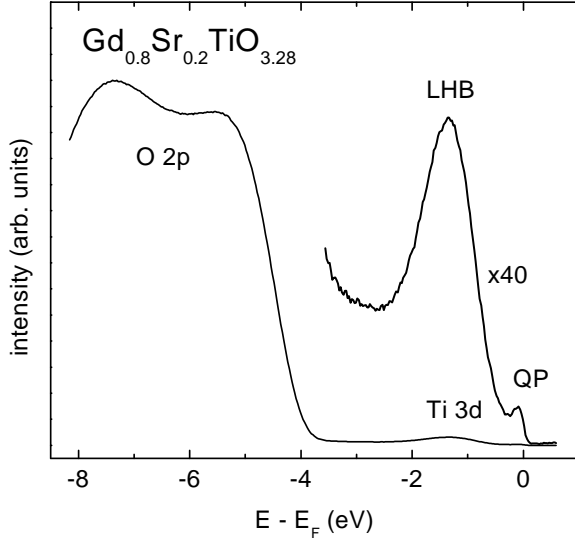


FIG. 1: UPS valence band spectrum of $\text{Gd}_{0.8}\text{Sr}_{0.2}\text{TiO}_{3.28}$. The spectrum has been corrected for He I_{β} satellite emission. The Ti 3d-derived part of the spectrum decomposes into the lower Hubbard band (LHB) and a quasiparticle peak (QP) at the Fermi level.

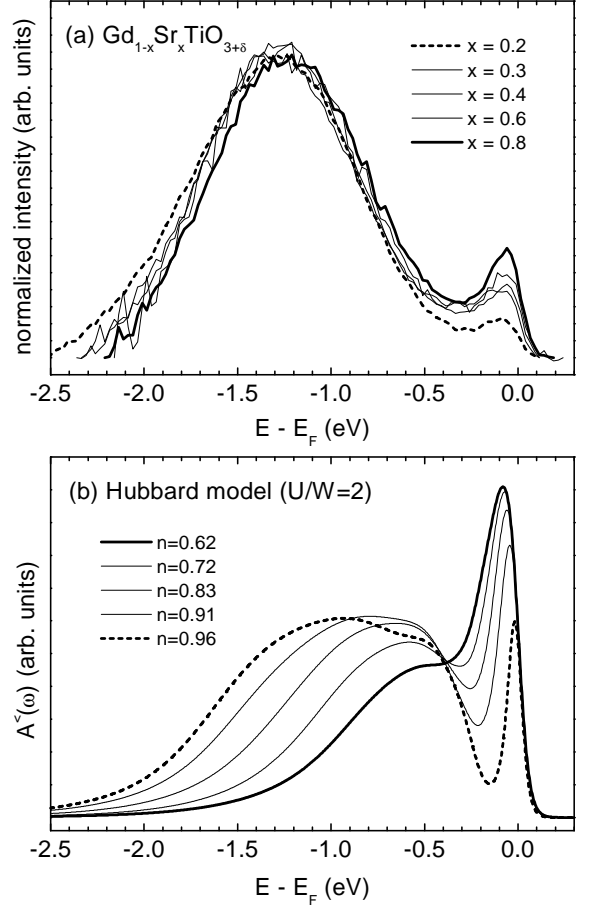


FIG. 2: (a) Ti 3d spectra of $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ with varying Sr-doping. For better clarity an inelastic background is subtracted. The spectra are normalized to same integral Ti 3d weight. (b) Theoretical photoemission spectra $A^{<}(\omega)$ calculated for the Hubbard model at various band filling factors n . The ratio of on-site Coulomb energy U and band width W is chosen as $U/W = 2$, with W set to 2 eV. See text for further details.

($x = 0.8$, but still within the metallic regime of the phase diagram) and strongly loses its spectral weight relative to the LHB as one approaches the Mott transition.

In Fig. 2(b) we display the electron removal part of the spectral function of the single-band Hubbard model as function of the band filling n , calculated within dynamical mean-field theory (DMFT)^{4,15} using the numerical renormalization group (NRG) method.¹⁶ The theoretical spectra have been broadened by the experimental resolution. They nicely reproduce the two peak structure of the measured UPS spectra. Another qualitative agreement between theory and experiment is the gain of quasiparticle weight for increased hole-doping. However, there is also an important qualitative discrepancy concerning the doping dependence of the peak energies. In the Hubbard model the quasiparticle peak shifts into the LHB with

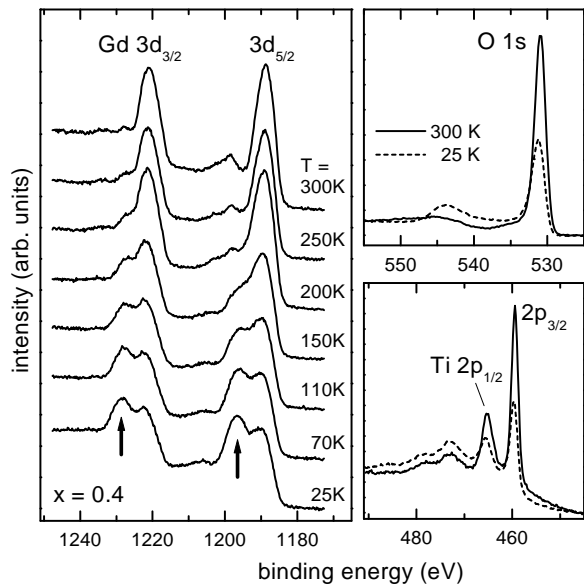


FIG. 3: XPS core level spectra of $\text{Gd}_{0.6}\text{Sr}_{0.4}\text{TiO}_{3.28}$. Left panel: Temperature-dependence of the Gd 3d spectra. Note the evolution of an additional structure (denoted by arrows) below 200 K. Right panels: O 1s and Ti 2p spectra of the same sample at room temperature (solid line) and 25 K (dashed line).

increased doping, or rather, with all energies referenced to the Fermi level E_F , the LHB peak moves closer to the Fermi level. In the theoretical spectra of Fig. 2(b) this shift amounts to almost 1 eV from $n = 0.96$ to 0.62. In contrast, in our UPS spectra the energy position of the LHB peak is completely independent of doping, consistent with photoemission results obtained on other doped titanates.^{9,10,13} One may wonder, if this discrepancy is an artefact of the single-band Hubbard model used here, whereas in the perovskite titanates the Ti 3d electrons have an added orbital degree of freedom as they move in a t_{2g} triplet of bands. There is however theoretical indication that the doping-dependent relative energy shift of LHB and quasiparticle peak is preserved in multiband Hubbard models.¹⁷

Rather, the observed disagreement may originate in an inhomogeneous sample composition which we infer from a detailed analysis of our XPS core level spectra. As an example, Fig. 3 shows the Gd 3d spectrum of a $x = 0.4$ sample, measured as function of temperature between 300 and 25 K. At room-temperature we observe the clean multiplet structure of trivalent Gd.¹⁸ Upon lowering the temperature (starting between 200 and 150 K) a gradual shift of spectral weight to higher binding energy occurs until at the lowest temperatures additional structures have developed (denoted by arrows in Fig. 3). A detailed analysis of the low temperature lineshape indicates that it can largely be understood as a superposition of the original room-temperature spectrum and an identical

replica shifted by ~ 9 eV to higher energy. Temperature-dependent line splitting and concomitant energy shifts were found for *all* core levels. As examples Fig. 3 also contains the O 1s and Ti 2p spectra.¹⁹ Furthermore, the effect was observed for all samples studied here except for $x = 0.8$.

The peculiar temperature dependence of the core level spectra can be explained in a quite natural way, if we assume an inhomogeneous doping concentration, *i.e.* a decomposition of our ceramic sample into metallic and insulating domains. In this case the doping parameter x represents only the average composition. At low temperatures the insulating fraction cannot compensate the photo-induced loss of electrons and will charge up, thereby leading to an apparent shift of the (partial) spectra to higher binding energy. With increased temperature thermally activated charge carriers help to reduce the charging in the non-metallic parts until eventually their core level energies approach those of the metallic phases. The absence of charging effects at a nominal doping of $x = 0.8$ indicates that this sample consists only of metallic phases (though it may still be inhomogeneous) and that the insulating fractions at lower x belong to the Gd-rich Mott-Hubbard insulator phase.

The chemical phase separation suggested by the XPS data is confirmed by energy dispersive x-ray microana-

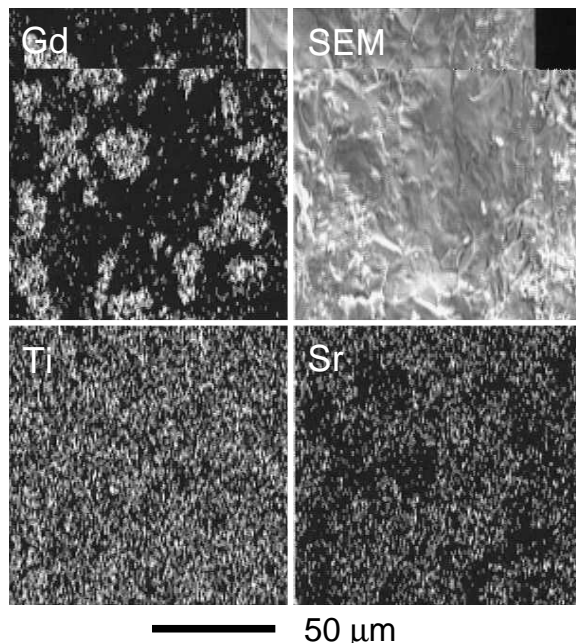


FIG. 4: Scanning electron micrograph of a scraped surface of polycrystalline $\text{Gd}_{0.7}\text{Sr}_{0.3}\text{TiO}_{3.3}$, measured with a primary electron energy of 20 keV (upper right panel). Also shown are the elemental maps for Gd, Ti, and Sr simultaneously obtained by EDX. White (black) areas denote high (low) concentration.

lyis (EDX) using a scanning electron microscope. Figure 4 shows elemental maps taken on the $x = 0.3$ (nominal value) sample. The Gd signal displays a highly inhomogeneous distribution which anticorrelates with the Sr density, *i.e.* Gd-rich regions coincide with Sr-poor ones and *vice versa*. In comparison, Ti appears to be rather evenly distributed over the sampled area. This gives independent evidence that the doping concentration strongly fluctuates inducing a spatial segregation into metallic and (Mott) insulating phases. Similar EDX maps were obtained from our other samples.

The fact that the spatial phase separation observed here has gone undetected in measurements of the bulk properties of the same samples¹⁴ suggests that it occurs only on the grain surfaces of the polycrystalline material. The thickness of the inhomogeneous surface layer must be at least of the order of the XPS probing depth (30...50 Å). The observation of inhomogeneities by EDX (sampling depth $\sim 1\mu\text{m}$) indicates that it is probably much larger.

As a consequence of these findings we must also conclude that the UPS valence band spectra presented above *do not* reflect the intrinsic electronic structure of single-phased material. They rather represent superpositions of spectra corresponding to the individual doping profile of each sample. Even though we did observe trends in the Ti 3d spectra with nominal doping x , the true doping dependence of the intrinsic spectra will thus be strongly obscured. This may be one possible explanation for the observed discrepancy to the Hubbard model, namely for the absence of relative energy shifts between LHB and quasiparticle band in our UPS spectra.

As mentioned before, our valence band data on $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$ reproduce those obtained from other

doped titanates.^{9,10,13} As these studies also employed polycrystalline samples, they may suffer from the same problems encountered here. Unfortunately, they do not give sufficient information in order to allow an assessment of their sample homogeneity. This implies that the photoemission data on the doping effects in these compounds presently available in the literature may not be of sufficient quality to allow a detailed and reliable comparison to theoretical spectra. Based on our present findings we strongly advocate the use of *single crystals* for further photoemission studies of the doping-induced MIT in titanates and related perovskites, because for such samples it is much easier to ensure and characterize sample homogeneity. We emphasize that this does not automatically imply that the surface electronic structure probed by photoemission is identical to that of the volume. In fact, recent studies on vanadates indicate substantial differences between surface and bulk.^{20,21}

In summary, we have presented the first photoemission data on the doping dependence of $\text{Gd}_{1-x}\text{Sr}_x\text{TiO}_{3+\delta}$. The Ti 3d part of the valence band is found to be in partial qualitative agreement with Hubbard model calculations, but also displays notable discrepancies to theory. From our XPS and EDX results we conclude that the surfaces of the polycrystalline samples are chemically inhomogeneous, thereby questioning the intrinsic character of the valence band spectra. Further studies require the use of high-quality single crystals.

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